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The Iodine Coulometer and the Value of the Faraday

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THE IODINE COULOMETER AND THE VALUE OF THE FARADAY

BY

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B. A. McMaster University, 1907

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Stuart Jeffery Bates

ENTITLED The Iodine Coulometer and the Value of the Faraday

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Doctor of Philosophy

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The present investigation was undertaken in the fall of 1910 at the suggestion of Professor E. W. Washburn, and has been carried on at the Chemical Laboratory of the University of Illinois during the academic years 1910-11 and 1911-12.

I wish to thank Professor Washburn for his kindly interest and assistance during the progress of this work.

THE IODINE COULOMETER AND THE VALUE OF THE FARADAY.

Introduction:

Although Faraday's law of electrochemical change has been universally accepted for many years, there still exists considerable uncertainty regarding the exact value of the faraday, or the electrochemical equivalent. Although theoretically any chemical reaction which can be brought about by means of the electric current, may be employed for the determination of the value of the faraday, as a matter of fact very few reactions have been studied in this connection and the value at present accepted for this constant is practically based upon measurements with a single electrochemical reaction, the deposition of silver from an aqueous solution of one of its salts. It must be admitted that for such an important and universal physical constant as the faraday, this is a most unsatisfactory state of affairs, and when we add to this the fact that the particular reaction which has been chosen for the purpose is known to be affected by numerous sources of error and uncertainty which have not been entirely removed by years of laborious investigation participated in by many chemists and physicists, it must be apparent to

all that serious consideration should be directed to the problem of discovering some other electrochemical reaction which will fulfill the exacting requirements necessary for a successful determination of the faraday, more perfectly than does the reaction which occurs in the silver coulometer.

Recent work on the silver coulometer, in particular that done at the Bureau of Standards, in Washington, has called in question some of the conclusions previously accepted. Hence, although this subject was exhaustively reviewed by Foerster[1] in 1910, it will be found advantageous to discuss some of the sources of error and uncertainty in the silver coulometer and to review some of the results obtained by the use of other coulometers which have been hitherto employed or suggested as applicable to this problem, in order to present more clearly the purpose and results of the present investigation.

The Silver Coulometer.

The large amount of study which this coulometer has received from so many investigators has naturally arisen from the fact that the international ampere is defined in terms of the mass of silver deposited per second under more or less definite physical and chemical conditions. The silver coulometer is apparently the only one receiving serious consideration at the present time, being in fact the subject of extended investigations through the cooperation of the leading national physical laboratories of the world.

The uncertainty in the value of the faraday as determined by means of this coulometer arises from the fact that it is not yet possible to determine accurately the weight of silver which reacts according to the equation,

$$Ag^{+} + (-) = Ag$$

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1) Zeit. physik. Chem., 76, 643 (1910).

when a known quantity of electricity passes through the coulometer. Many investigations have not satisfactorily explained the effect of slight variations in the physical or chemical conditions upon tne mass of silver deposited at the cathode. Neither have they shown the proper conditions to employ in order to determine the true electrochemical equivalent of silver. If the above were the only reaction taking place during the passage of the current, the loss in weight at the anode should be equal to the gain in weight at the cathode. However, the results obtained in this manner from the anode and from the cathode respectively do not agree [1], and a study of the reactions taking place at the anode does not promise consistent results.

As a partial explanation it has been suggested that under certain conditions complex ions such as Ag_2^+ are formed at the anode. Some of these complex ions may be deposited on the cathode and consequently the gain in weight is greater than that corresponding to the simple reaction given above. Another complicating factor is due to the inclusion of solution by the silver deposited on the cathode. This is known to be quite appreciable, yet its amount appears to vary considerably according to conditions. Richards [2] proposed to eliminate, or at least to diminish the effects due to the first of these disturbing influences, by placing the anode in a porous cup. By keeping the level of the liquid inside the cup lower than that outside, the slow current of solution which is moving into the cup allows few if any of the complex ions to enter the outer vessel and give up their charges at the cathode. The amount of silver deposited in the porous cup coulometer has been found to be less than that deposited in the filter paper type. This difference has been variously estimated by different observers. The following table shows these differences

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1) Richards and Heimrod. Proc. Am. Acad., 37, 434 (1902).
2) Richards, Collins and Heimrod. Proc. Am. Acad., 35, 123 (1899).

in per cent. With the exception of the data obtained by Jaeger and von Steinwehr[1] the table is taken from the review by Foerster[2].

Table I

Richards and Heimrod	1st series	0.081
	2nd series	0.033
	3rd series	0.058
Guthe		0.048
Watson		0,026
Van Dijk	1st series	0.028
	2nd series	0.020
Smith, Mather and Lowry		0.001
Jaeger and von Steinwehr		± 0.000

Smith, Mather and Lowry[3] employed an unusually large bulk of solution in their coulometers and, as they pointed out, this had a tendency to keep down the concentration of the complex silver ion and hence to retard its deposition. Another cause for this small difference between the mass of silver deposited in the filter paper coulometer and that deposited in the porous cup type is doubtless found in the fact that they paid more attention to the purity of the silver nitrate employed than did most of the other investigators. Using silver nitrate solutions which were not of known purity they found that the porous cup coulometer gave a deposit 0.03 per cent. lighter than did the filter paper coulometer[4], which agrees with the observations of the other observers as shown by the above table. Their results would tend to indicate that the chief

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1) Zeit. Instruementenk. 28, 366 (1908).
2) loc. cit. p. 660.
3) Phil. Trans., 207, A, 545 (1908).
4) loc.cit. 582.

difference between the two types of coulometers is not due to the formation of Ag_2^+ ions at the anode.

It has been found by Eisenreich[1] that solutions of silver fluoride and of silver nitrate which give excessive deposits of silver, also reduce potassium permanganate solution. This was interpreted as proving the presence of the complex ion. It was also found that at a higher temperature the reducing power of the solution was greater, which was explained as due to the shifting of the equilibrium,

$$Ag^+ + Ag = Ag_2^+$$

from left to right with rising temperature. This would account for the increased deposit of silver in certain types of coulometer at higher temperatures.

The latest work at the Bureau of Standards at Washington, however, is held to contradict the complex ion theory[2]. "No evidence was found of reducing substances at the anode, such as sub-silver nitrate." The results obtained by the other investigators is explained by the fact that filter paper contains oxycellulose. This dissolves giving a reducing solution, which results in the formation of colloidal silver. Instead of diminishing the disturbing influences as would be the case on the complex ion theory, it is found that the use of two or three thicknesses of filter paper increases the weight of the silver deposit[3].

The determination of the purity of the silver deposit is evidently of great importance in the calculation of the faraday. If some of the silver nitrate solution were occluded a loss in weight should result in strongly heat-

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1) Zeit. physik. Chem., 76, 697 (1910).
2) McDaniel, Science, N. S., 34, 160 (1911).
3) Vinal, Science, N. S., 34, 31, (1911).

ing the deposit of silver. Various estimations which have been made of this loss show poor agreement. Rayleigh and Sidgwick[1] found that with well washed deposits there was a loss in weight of 0.01 - 0.02 per cent. on heating to the verge of redness. Richards and Heimrod[2] dried the deposits to constant weight at 160° C and then heated them over an alcohol flame. The loss in weight varied from 0.003 to 0.030 per cent., the mean value was 0.018 per cent. Van Dijk[3] found that after washing and drying at 150° C there was no further loss in weight on reheating to 500 - 600° C. Smith, Mather and Lowry[4] heated their silver deposits to constant weight in an electric oven at 160° C. Eight deposits were then heated to 240° C and three to 400° C, but in no case was there a loss in weight. It is quite possible, however, as Richards[5] has pointed out that the temperatures used in the last two investigations were not sufficient to soften the silver and allow the water vapor to escape.

In order to investigate both the quantity and the quality of the material occluded in the silver deposit, Duschak and Hulett[6] have examined the deposit and determined the dependence of the amount of impurity upon dissolved gases. They found that with proper care the porous cup coulometer was reproducible to one part in 100,000 but that the deposit obtained in the usual way was 0.007-0.008 per cent. heavier than that obtained from an oxygen free solution in vacuo or in an atmosphere of nitrogen. This result does not agree with the investigations of Schuster and Crossley[7] and of Meyers[8] both of whom state

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1) Phil. Trans. 175, 411 (1884).
2) Proc. Am. Acad. 37, 435 (1902)
3) Arch. neerl. 10, 287 (1905).
4) loc. cit., p. 570.
5) Proc. Am. Acad. 44, 91, (1909).
6) Proc. Am. Electrochem. Soc. 12, 257 (1907).
7) Proc. Roy. Soc. 50, 344 (1892).
8) Wied. Ann. 55, 288 (1895).

that a deposit obtained in vacuo is the heavier. Recently Jaeger and von Steinwehr[1] at the Physikalisch-Technischen Reichsanstalt, found that the deposits in air and nitrogen did not differ by more than 2 parts in 100,000, that obtained in nitrogen being if anything the heavier[2].

Duschak and Hulett confirmed the difference as found by them by an examination of the silver deposits. In all cases it was found that the silver deposit after being dried to constant weight at 160 - 5°, still contained water and silver nitrate. By heating the deposits in vacuo they found that a gas was given off up to 650° C. The quantity of each impurity was ingeniously determined and the following table shows the results[3].

Table II

	Deposits in air.	Deposits in vacuo.
Water	0.0094 per cent.	0.0054 per cent.
Silver nitrate	0.0041 " "	0.0030 " "
Total	0.0135 " "	0.0084 " "

The observed difference in weight of the deposit obtained in air and in vacuo was 0.007 - 0.008 per cent., while the analysis shows a difference of 0.0051 per cent. Hence there is some factor as yet unaccounted for which causes the deposit in air to be at least 0.002 per cent. heavier than in vacuo. What may be the total effect of this unknown factor on the weight of the deposit there is at present no accurate means of determining.

While the possible influences of the complex silver ion and of included liquid upon the weight of the deposit have received the major portion of the attention of investigators, recent work at the Bureau of Standards has shown

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1) Loc. cit. 353.
2) It was also found in two experiments that the deposit obtained in hydrogen was 0.14 and 0.25 per cent. heavier than that obtained in air.
3) Loc. cit. p. 291

that these are by no means the only complicating factors. The unsatisfactory condition of our present knowledge of the silver coulometer is well summed up by the following quotation from an article by Rosa [1]. "Further study at the Bureau of Standards show complexities due to the presence of filter paper which astonished chemists, and three years of continuous work have not answered all the questions which have arisen as to the effect of traces of impurity or traces of acid or alkali in the salt, or slight variation in the physical condition of the anode, or the volume and concentration of the electrolyte, or the density of the current, or the influence of dissolved gases."

In Table III are given values of the electrochemical equivalent of silver in milligrams per coulomb as found in some of the more careful absolute determinations.

Table III

		Milligrams per coulomb.
Rayleigh and Sidgwick [2]	1884	1.1179
F. and W. Kohlrausch [3]	1884	1.1183
Pellat and Potier [4]	1890	1.1192
Kahle [5]	1898	1.1183
Pellat and Leduc [6]	1903	1.1195
Van Dijk and Kunst [7]	1904	1.11823
Guthe [8]	1906	1.11773
Smith, Mather and Lowry [9]	1908	1.11827

1) Science, N. S. 35, 11 (1912)
2) Phil. Trans. 175, 411 (1884).
3) Wied. Ann. 27, 1 (1886).
4) J. Physique, 9, 381 (1890)
5) Zeit. Instruementenk. 18, 229 (1898).
6) Comp. rend. 136, 1649 (1903).
7) Ann. Physik. (4), 14, 569 (1904).
8) Bull. Bureau of Standards, 2, 70 (1906).
9) Phil. Trans. 207, 579 (1908).

The investigation of Smith, Mather and Lowry was the most extensive and most complete of any of these; they estimated their result, 1.11827, to have a probable error of 2.4 parts in 100,000. However as has been noticed above they did not sufficiently investigate the question of included liquid. While their experiments showed that the filter paper coulometer and the porous cup type were each reproducible to one or two parts in 100,000 and under certain conditions agreed with one another as closely, the faraday as calculated from their value for the electrochemical equivalent of silver may be as much as 0.02 per cent. too low. This will be seen from the following considerations.

These investigators found a variation of over 0.01 per cent. caused by different methods of treating the porous cups which were used in the porous cup type of coulometer. All the cups were cleaned with KCN and HNO_3 and then thoroughly washed. Some were soaked for several days in water. The average of 13 determinations of the electrochemical equivalent of silver with these cups was 1.11814 mg. per coulomb. It was found that heating the cups in an electric furnace gave more consistent results. The average of nine determinations gave the value 1.11828 which is practically identical with that (1.11827) obtained by the use of the large filter paper type.

The fact that in the hands of different investigators the difference between the weight of silver deposited in the filter paper type and that deposited by the same current in the porous cup coulometer varies so greatly [1], and the results on the weight of the deposit of a slight variation in the method of treating the porous cup show the risk of comparing the results of one investigator with those of another. The deposits of silver obtained by Smith, Mather and Lowry undoubtedly contained some included liquid. While

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1) See Table I.

the amount of this liquid cannot be at all satisfactorily calculated, some idea of its amount may be estimated. Richards who does not describe in detail the treatment which his porous cups received, found a mean of 0.018 per cent. included liquid. Duschak and Hulett who kept their porous cups in water when not in use found an inclusion of 0.0135 per cent. The value of the electrochemical equivalent of silver which Smith, Mather and Lowry obtained with cups similarly treated is 1.11814. Hence it is possible that the true value may be lower than 1.11800.

The higher value (1.11827) has however been rendered more probable by some preliminary work at the Physikalisch-Technischen Reichsanstalt[1], and by a recent investigation of F. Kohlrausch[2] who concludes that the value 1.1183 obtained in 1884 (see Table III) was not more than 0.002 per cent. too great. The value generally accepted for the faraday is that calculated from the work of Smith, Mather and Lowry, that is,

$$F = \frac{107.88}{1.11827} \times 1000 = 96{,}473 \text{ coulombs.}$$

The situation with regard to the silver coulometer may be summed up as follows: A given investigator working with given materials and under given conditions can obtain results with the silver coulometer which are reproducable to a few thousandths of one per cent. It is doubtful, however, if another investigator could duplicate the results with this degree of precision and it is also doubtful if the same investigator starting with another lot of materials could duplicate his previous conditions with sufficient accuracy to obtain the same result. Moreover, slight variations in materials and conditions produce very pronounced differences in the results and it is absolutely impossible (and always will be) to determine with certainty by a study of the sil-

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ver coulometer alone what set of conditions must be complied with in order to obtain the correct value of the faraday. We are not at present, justified, in believing that we know the faraday to much better than 0.1 per cent.

The Copper Coulometer.

The copper coulometer has been the subject of a number of investigations. The work of Richards, Collins and Heimrod[1] may be considered as superseding that of earlier investigators. They found that two most important factors influenced the result in opposite directions. (1) "Metallic copper slowly dissolves in an acid solution of cupric sulphate. - - - The losses of weight of the plates was found to be roughly proportional to the respective areas of the plates, if the volume of solution were large". (2) "Plates of copper immersed in neutral solutions of cupric sulphate always gain in weight, becoming coated with a film of cuprous oxide".

The latter difficulty was eliminated by using a slightly acid solution, while the influence of the former was reduced by employing a low temperature and working in an atmosphere of hydrogen. Assuming then that the rate of solution of the metallic copper varies directly as the area of the plate, it was possible by using plates of different areas as cathodes in two coulometers in series, to extrapolate to the increase in weight of a plate of zero area, i.e. to calculate what would have been the gain in weight of the cathode if none of it had dissolved.

No investigation appears to have been made to determine the presence or absence of moisture in the copper deposited. However, since a copper deposit is much smoother than a silver deposit, it is probable that it contains less

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1) Proc. Am. Acad. 35, 123 (1899).

moisture.

Assuming that the increase in weight of the cathode as calculated in the manner indicated above is due entirely to the discharge of cupric ions, the electrochemical equivalent of cupric copper was found to be 0.32929 milligrams per coulomb[1]. This value agrees (within 0.005 per cent.) with that calculated from atomic weights of the metals and the electrochemical equivalent of silver (1.1175 mg. per coulomb) as calculated by these investigators from their comparison of the filter paper and porous cup coulometers, assuming 0.018 per cent. of moisture to be enclosed in the silver deposit.

From the facts mentioned in the discussion of the silver coulometer, it is seen that to obtain an accurate measure of the current by means of the filter paper coulometer seemingly minor details must be very carefully duplicated. It is scarcely likely that the current as calculated by means of the silver coulometers used in this investigation was known to within 0.03 per cent. of its true value[2]; the uncertainty in the value of the faraday as calculated from these data is then as much as 0.03 per cent. The value given on the basis of the 1902 atomic weights (Cu = 63.60, Ag = 107.93) was 96,580 coulombs. Recalculated for 1912 atomic weights this value becomes 96,535 $\pm$ 30 coulombs.

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1) Richards and Heimrod. Proc. Am. Acad. 37, 438 (1902).
2) The reproducibility of the filter paper coulometer in the hands of these investigators was 0.023 per cent. This value was calculated by Foerster (Loc cit. p. 660) from the results of experiments 12-17. Proc. Am. Acad. 35, 135 (1899).

The Iodine Coulometer.

The iodine coulometer has been studied by a number of investigators;[1] but for the present purpose the results of Kreider and Gallo alone need be considered; the earlier investigators did not claim an accuracy greater than 0.5 per cent.

Kreider surrounded the cathode with a solution of hydrochloric acid and the platinum anode with a solution of potassium iodide. The iodine formed at the anode was titrated by means of sodium thiosulphate. The amount of iodine liberated in two or three coulometers in series agreed to within 0.01 to 0.02 per cent. In two experiments the iodine coulometer was compared with a silver coulometer of the filter paper type. The author finds that the iodine liberated was from 0.06 to 0.09 per cent. more than that calculated from the silver coulometer. The atomic weights which were employed in this calculation are not given, neither is there any data from which they may be discovered. The atomic weights for 1904 were Ag = 107.93, I = 126.85; for 1905 Ag = 107.93, I = 126.97. The paper is dated June 1905, hence it is quite possible that the atomic weights for 1904 were employed. If this were the case the amount of iodine formed, calculated on the basis of the atomic weights for 1912, was from 0.04 to 0.01 per cent. too small. This result is in better agreement with the observations of other investigators.

Gino Gallo made an attempt to determine the atomic weight of iodine by means of a comparison of the silver and iodine coulometers, in the hope that the results might throw some light upon the iodine-tellurium anomaly in the periodic system.

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In the apparatus employed by this investigation, the platinum electrodes (4 square millimeters) were placed in separate limbs; the cathode at the bottom of one tube, the anode somewhat more than half way up the other. Before filling the apparatus with the potassium iodide solution, the cathode was surrounded with solid iodine. During the passage of the current considerable hydrogen was evolved at the cathode but the hydroxyl ion formed was neutralized by the iodine. In order to prevent diffusion of the iodine from cathode to anode, the two limbs were connected by two small tubes (4 mm. diameter) both of which dipped into a wide mouthed bottle. At the completion of a run a stop-cock at the bottom of the anode limb was opened. This let the anode solution into a flask to be titrated with sodium thiosulphite. A current density of 0.1 ampere per sq. cm. was employed, the amount of iodine produced being about 0.3 gram in each run.

Assuming that the theoretical quantity of each element was freed from the ionic state by the passage of the current, he found the atomic weight of iodine to be 126.89 (Ag = 107.93) as the result of 24 determinations. The maximum deviation was 0.075 per cent., the average deviation 0.021 per cent. Calculated on the basis of the present value for silver (107.88), iodine becomes 126.83, a difference of 0.07 per cent. from the accepted value, 126.92.

On the other hand we may assume that the current frees the theoretical amount of iodine in the iodine coulometer, and consider that the silver coulometer measures the amount of electricity which has passed. Gallo used porous cup silver coulometers and employing Richards' and Heimrod's data, made a 0.018 per cent. correction for included moisture. The effect of this correction was to lessen the discrepancy between the silver and iodine coulometers, and hence if we compare these results with those of Smith, Mather and Lowry who

made no correction for moisture, we see that the values for the faraday as calculated from Gallo's investigation on the iodine coulometer, and from the result of the work of Smith, Mather and Lowry on the silver coulometer differ by 0.09 per cent. On this basis the iodine coulometer gives the value 96,560 coulombs. The uncertainty in this figure due to the difficulty in reproducing the exacting conditions in connection with the silver coulometer is at least 0.02 per cent.

The Knall-gas Coulometer.

Lehfeldt[1] measured the combined volumes of hydrogen and oxygen evolved when a known current was passed through an aqueous solution of an electrolyte; from this data he calculated the value of the faraday. The current was determined by means of the Weston Standard Cell and standard resistances; the author estimated that the quantity of electricity which passed through the coulometer was known to 0.01 per cent.[2]

In the coulometer, solutions of some twelve different electrolytes were used. It was found that with a given current, solutions of sodium sulphate and of potassium bichromate gave practically the same volume of gas, while solutions of other electrolytes did not give as much. The mean of 16 determinations with solutions of the two electrolytes mentioned above was 0.17394 cc. of gas evolved per coulomb. The average deviation was 0.027 per cent., the maximum was 0.058 per cent. The value of the faraday calculated on the assumption that the theoretical quantity of gas is evolved from these solutions is 96.590 coulombs. This value should be considered as an upper limit to the faraday, because no attempt was made to prove the above assumption,

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and if it is not true, the volume of gas evolved was too small.

In the following table are summed up the most probable values which have been obtained[1] for the faraday from a study of the various coulometers which have been investigated.

Table IV

Coulometer			Faraday in Coulombs
Silver	Smith, Mather and Lowry	1908	96,473
Silver	Jaeger and von Steinwehr	1908	96,473
Copper	Richards, Collins and Heimrod	1902	96,535
Iodine	Gino Gallo	1906	96,560
Knall-gas	Lehfeldt	1908	96,590

The value obtained with the silver coulometer is the most precise but as will appear later it may be in error by as much as 0.05 per cent.

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1) Recalculated where necessary using 1912 atomic weights.

Choice of an Element to be Used in Determining the Faraday.

It is evident from an inspection of tables III and IV, and from the above discussion, that the uncertainty in the value of the faraday is considerable. It would seem that this constant might be more exactly determined by the careful investigation of a coulometer employing some element other than silver, which is the only element whose electrochemical equivalent has been the object of extensive investigations.

The element chosen for this purpose must fulfill certain requirements and should, if possible, offer certain advantages.

1. The atomic weight of the element must be accurately known.

2. The product of the reaction must be capable of being accurately and if possible rather easily and rapidly determined.

3. The reaction which takes place at the electrode must be clean cut and entirely free from interfering side reactions.

The direction in which any electrochemical reaction proceeds depends upon the direction of the current of electricity. Such a reaction will take place in one direction at the cathode and in the opposite direction at the anode when a current is passed through a cell constructed in the proper manner. An element which would permit an accurate quantitative and independent estimation of the course of the reaction to be made from a study of the changes at the two electrodes would enable the presence or absence of side reactions to be proved. A coulometer of such a type would contain a check within itself, and might be used for calculating the true value of the faraday.

4. The complicating influences in the silver coulometer cause the weight of the deposit to be too great, hence the value of the faraday obtained by this means may be taken as a lower limit. It would be advantageous to employ

an element which, if admitting of any error, would give too high a value for the faraday, so that definite limits might be obtained for this constant.

5. Since all deposits will be more or less subject to the same disturbing influences as have been observed in the silver coulometer, (more particularly inclusion of solution and formation of complex ions) a non-metallic element offers advantages over a metal especially if it be not deposited upon the electrode, but simply formed in solution, thus entirely obviating errors due to inclusion or adsorption.

6. An element with a high electrochemical equivalent is desirable, since whether weighed directly or determined indirectly, the calculation of the faraday is based ultimately upon the weight of the element itself.

Iodine very satisfactorily satisfies the above conditions. The atomic weight of this element is one of the most accurately known. By a careful determination of the ratios silver to iodine pentoxide and silver to iodine, Baxter[1] found the atomic weight of iodine to be 126.913. This element also serves particularly well for calculating the total effect of the complicating influence in the silver coulometer since the ratio silver to iodine has been carefully studied.

The conditions for the titration of iodine with arsenious acid have been carefully studied by Washburn[2]. From the equilibria involved it was calculated and experimentally verified that an accuracy of 0.002 per cent. is attainable.

A solution of an iodide to which iodine has been added contains iodide and triiodide ions. When a current of electricity is passed through such a solution the reaction

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1) J. Am. Chem. Soc., 32, 1591 (1910).
2) J. Am. Chem. Soc., 30, 31 (1908).

$$I_3^- + 2(-) = 3\,I^-$$

takes place in the direction from left to right at the cathode and in the reverse direction at the anode. A cell then in which the electrodes are surrounded by such a solution should contain the same total amount of iodine before and after the passage of an electric current. By separating the electrodes and the solutions surrounding them by a conducting solution of an iodide, the change found in the amount of iodine at the two electrodes should be the same. At the electrode most easily studied (i.e. the anode) any error which may arise will be such that too little iodine is formed, and hence an upper limit will be found for the faraday.

The element iodine forms an anion and has one of the largest electrochemical equivalents. The advantages arising from these properties were mentioned above.

Since iodine then offers particular advantages for studying the value of the faraday, an investigation of the iodine coulometer was undertaken. The changes in the amount of iodine at the cathode and at the anode were studied, the reproducability of the results determined and a preliminary comparison made between the iodine coulometer and the silver coulometer.

Determination of the Iodine.

The iodine was determined by means of a standard solution of arsenious acid. The most favorable conditions for this titration have been studied by Washburn[1]. Since the concentration of the various reacting substances at the end of the titration is very different from that used by him and since some of the data employed in the calculations have since then been redetermined, it will be necessary to repeat these calculations for the conditions employed in this investigation.

The reaction by means of which the iodine is determined may be written as follows,

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3\,I^- \quad (1)$$

By making the hydrogen ion concentration sufficiently small this reaction may be driven as completely as desired towards the right. If it is made too small, however, disturbing influences arise due to the hydroxyl ion which reacts with the triiodide ion thus,

$$OH^- + I_3^- = HIO + 2\,I^- \quad (2)$$

and

$$6\,OH^- + 3I_3^- = IO_3^- + 8\,I^- + 3H_2O \quad (3)$$

The concentration of the hydrogen ion then must be so small that reaction (1) may be sufficiently complete, yet not so small that an appreciable amount of iodine will react according to equations (2) and (3).

Conditions were controlled so that at the end point of each titration, (whether analysis of anode or cathode solution or standardization of the arsenious acid solution) the concentrations of all substances present were approximately the same in each titration. In order to calculate the best hydrogen ion concentration it is necessary to know the concentration of these various reacting substances.

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1) J. Am. Chem. Soc., 30, 31 (1908).

The volume of the solution at the end point is about 625 cc.; 0.025 moles of iodine have been titrated and about 0.25 moles of potassium iodide are present. Hence we have the relation

$$I^- = 0.25 \times 1.6 \times 0.70^{1)} = 2.8 \cdot 10^{-1}$$

Assuming a desired accuracy of 0.001 per cent. in the titration of the iodine, not more than this per cent. of the arsenious acid used must remain unoxdized. That is, at the end of the titration,

$$H_3AsO_3 = 0.00001 \cdot 0.025 \cdot 1.6 = 4 \cdot 10^{-7}$$

The concentration of I_3^- necessary to give the proper colored end point with starch was determined by experiment. It was found that 0.2 cc. of a 0.01 N solution of iodine changes 625 cc. of the titrated solution from colorless to the color of the pink end point. Hence

$$I_3^- = 0.000002 \cdot 1.6 = 3.2 \cdot 10^{-6}$$

During the titration 0.025 mole of arsenious acid has been oxidized to arsenic acid. Hence the concentration of H_3AsO_4 may be calculated in terms of H^+ by combining the relation

$$(H_2AsO_4^-) + (H_3AsO_4) = 0.025 \cdot 1.6 = 4 \cdot 10^{-2}$$

with the ionization constant for arsenic acid

$$\frac{(H^+)(H_2AsO_4^-)}{(H_3AsO_4)} = 4.8 \cdot 10^{-3}$$

To calculate the concentration which HIO or IO_3^- may not exceed if an error not greater than 0.001 per cent. is introduced because of reactions (2) or (3), we note that the total quantity of iodine titrated is 0.025 mols. Hence the upper limit of HIO or IO_3^- is given by the relation,

$$HIO = IO_3^- = 0.000001 \cdot 0.025 \cdot 1.6 = 4 \cdot 10^{-8}$$

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1) It will be found that in the resulting solution the total equivalent electrolyte concentration is about 0.80. The degree of dissociation of the salts in this mixture will be assumed to be 0.70 per cent.

Calculation of the Upper Limit of the Hydrogen Ion Concentration.

The upper limit which the concentration of the hydrogen ion may have and reaction (1) still go to completion (within 0.001 per cent.) is calculated by substituting the various values given above in the equilibrium constant of reaction (1) and solving for H^+.

This equilibrium constant has been recently determined at 25° in this laboratory by Mr. E. K. Strachan and found to be $4.8 \cdot 10^{-2}$. That is

$$\frac{(H_3AsO_4) \cdot (H^+)^2 \cdot (I^-)^3}{(H_3AsO_3)(I_3^-)} = 4.8 \cdot 10^{-2}$$

The upper limit of the hydrogen ion concentration so obtained is $1.1 \cdot 10^{-4}$.

Calculation of the Lower Limit of the Hydrogen Ion Concentration.

The concentration which the hydroxyl ion may attain and yet cause no appreciable error is found by substitution in the equilibrium constants for reactions (2) and (3). The constant for reaction (2)

$$OH^- + I_3^- = HIO + 2\,I^-$$

may be obtained by means of the following relations;

$$\frac{(HIO)(I^-)\,(H^+)}{(I_2)} = 3 \cdot 10^{-13}\ ^{1)} \qquad (1)$$

$$\frac{(I_2)(I^-)}{(I_3^-)} = 1.3 \cdot 10^{-3} \qquad (2)$$

and $$(H^+)(OH^-) = 1.0 \cdot 10^{-14} \qquad (3)$$

Dividing the product of (1) and (2) by (3) gives

$$\frac{(HIO)(I^-)^2}{(I_3^-)(OH^-)} = 3.9 \cdot 10^{-2}$$

On substituting the values of (HIO), (I^-) and (I_3^-) previous calculated we obtain $2.4 \cdot 10^{-2}$ as the upper limit of the concentration of the hydroxyl ion, if an error not greater than 0.001 per cent. is to be introduced because of reaction (2).

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1) Bray and Connolly. J. Am. Chem. Soc., 33, 1486 (1911).

The equilibrium constant of reaction (3),

$$6OH^- + 3\ I_3^- = IO_3^- + 8\ I^- + 3H_2O,$$

has from other data been calculated[1] to be

$$\frac{(IO_3^-)\ (I^-)^8}{(OH^-)^6(I_3^-)^3} = 6 \cdot 10^{28}$$

On making the proper substitutions OH^- is found to be equal to $1.2 \cdot 10^{-4}$, which is a smaller value than that obtained for reaction (2).

Since the hydroxyl ion concentration may not exceed $1.2 \cdot 10^{-4}$, the hydrogen ion concentration may not be less than $8 \cdot 10^{-11}$. As an upper limit the value $1.1 \cdot 10^{-4}$ was found.

That is the hydrogen ion concentration of the solution at the end point may lie anywhere between the rather wide limits, $8 \cdot 10^{-11}$ and $1.1 \cdot 10^{-4}$. The value which was chosen as the best value was the geometric mean of these two, i. e. $9 \cdot 10^{-8}$, or the solution should be practically neutral. This may be accomplished by having present in the solution a mixture of Na_2HPO_4 and NaH_2PO_4 in the ratio of about two mols to one mol[2]. The presence of such a mixture will automatically keep the solution neutral, even if rather large quantities of acid or base are added to the solution. The necessary conditions at the end point were attained by adding to the reacting mixture such an amount of a stock solution of Na_2HPO_4 that six mols of this salt were added for every mol iodine to be titrated. The reduction of the iodine then gave two mols of hydrogen ion, which react with two mols of Na_2HPO_4 yielding two mols of NaH_2PO_4, thus giving at the end of the titration the desired ratio of two mols to one mol between the di- and monosodium phosphates.

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1) J. Am. Chem. Soc., 30, 35 (1908).
2) Loc. cit. p. 38

Purification of Chemicals and Preparation of Solutions.

Water. The water from which the various chemicals were recrystallized and which was used in making up all of the solutions was conductivity water obtained from a special still. The water was kept in "Non-sol" glass bottles.

Iodine. The iodine employed was Kahlbaums 'Resublimed' which was freed from chlorine, bromine, etc. either by subliming from a concentrated solution of potassium iodide, or by precipitation from such a solution by means of potassium permanganate and sulphuric acid. The iodine was thoroughly dried in a desiccator over sulphuric acid and sublimed in a current of dry air. That which was employed for standardizing the arsenious acid solution was then kept over sulphuric acid until it was required for use.

Potassium Iodide. The potassium iodide used was, except where indicated otherwise, obtained by recrystallizing J. T. Baker's 'Special' until it was no longer alkaline to phenolphthalein. The product was pure white and when dry remained so indefinitely. When protected from strong light, a saturated solution of the iodide remained colorless for at least twenty-four hours.

Arsenious Acid. The arsenious acid was obtained by recrystallizing Merck's product from conductivity water.

Sodium Hydroxide. The sodium hydroxide employed in preparing the standard arsenious acid solution was Kahlbaum's "mit Alkohol gereinigt in Stücken".

Starch Solution. The starch solution used as an indicator in the titration was prepared by grinding 6-7 grams of corn starch with a little cold water and adding to a liter of boiling water. After settling in a tall cylinder over night, the upper half of the solution was drawn off clear into test tubes stoppered with cotton wool and sterilized in an autoclave. Starch solutions was

thus prepared keep well for six weeks or two months, and give an end point color of the proper shade [1].

Sodium Phosphate Solution. This solution was prepared by dissolving J. T. Baker's C. P. disodium phosphate ($Na_2HPO_4 \cdot 12H_2O$) in about five times its weight of water. The solution was kept in a ten liter stock bottle from which the required amount was syphoned off and poured into the flask in which the titration was performed.

The Standard Iodine Solution. The standard iodine solution used at the cathode was prepared by dissolving about 680 grams of iodine and 840 grams of potassium iodide in 700 grams of water. This solution was kept protected from the light in a stock bottle into the neck of which was ground a delivery tube which reached to the bottom of the bottle. Air previously bubbled through a wash bottle containing some of the same solution was used to force the solution out of the stock bottle. To prevent loss of iodine or water vapor the end of the delivery tube and that of the tube through which pressure was applied were protected by means of glass caps. The arrangement is shown in Fig. (1). The solution was made up at least eight months before it was used for the experiments recorded below.

The dilute iodine solution, which was used only when the end point was overstepped with the arsenious acid, was 0.005 normal. It was prepared by weight from the above solution and was kept in a bottle into whose neck was ground a glass stopper which carried a Göckel automatic burette.

Standard Arsenious Acid Solutions. The standard arsenious acid solution was prepared by dissolving 530 grams of arsenic trioxide in a solution containing about 650 grams of NaOH (3 moles). When all the trioxide had dis-

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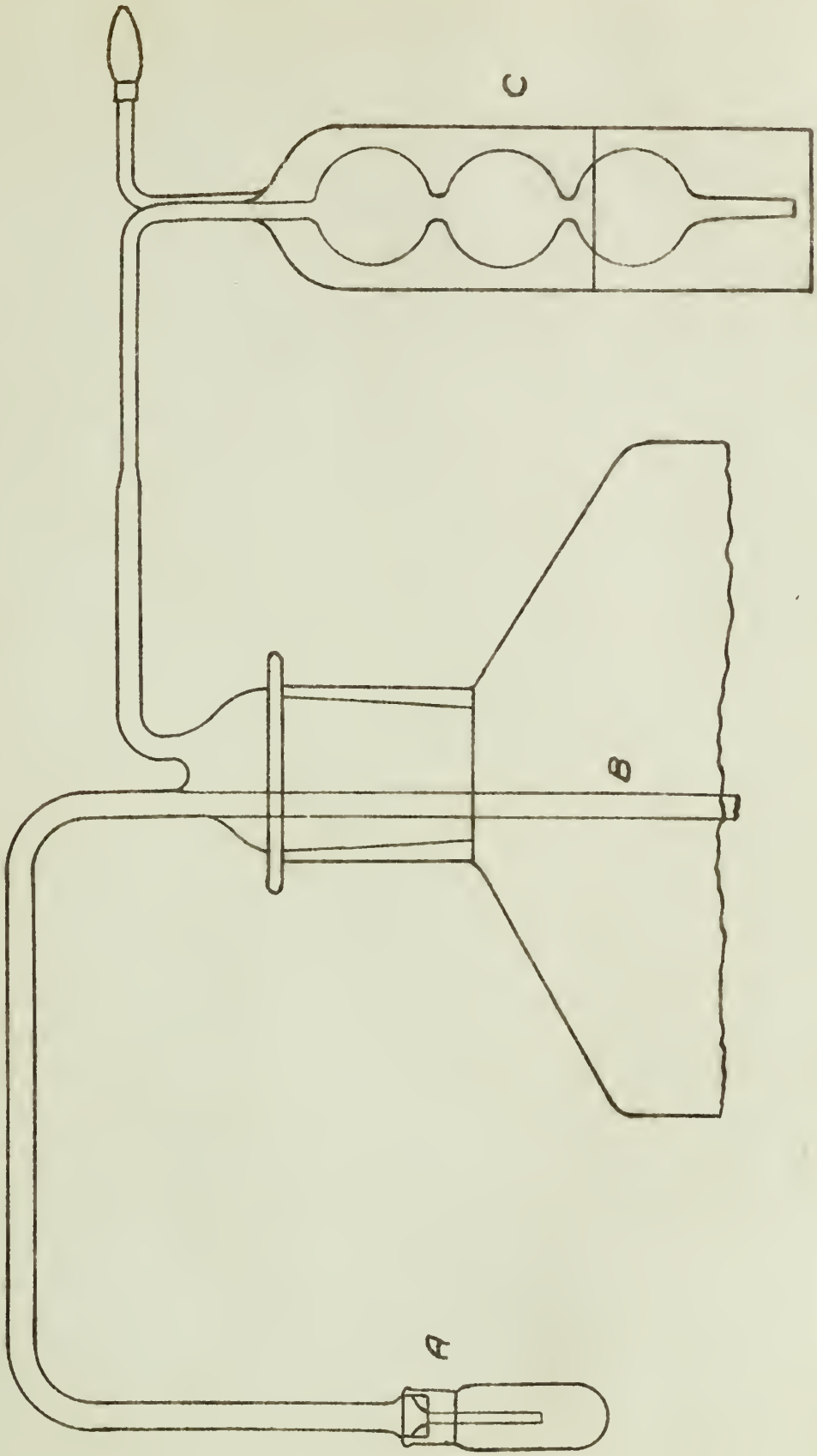


Fig. 1

solved, the solution was filtered through asbestos and diluted until it was approximately 0.9 weight normal.

At first an automatic burette was employed to deliver the arsenious acid solution into flasks to be weighed. With this arrangement most irregular results regarding the strength of the solution were obtained. It was noticed, however, that in general the solution tended to become weaker with time, indicating oxidation. The irregularity of the results may be explained by the fact that the burette was in general filled to the top before each titration, but was usually only a little more than half emptied. The other half of the solution which had become pretty well saturated with air, then lay for an indefinite period in the lower part of the burette till the next portion was drawn off. This portion of the standard solution then oxidized more rapidly than that in the stock bottle, and thus irregular results were obtained. The rate of oxidation of the stock solution was estimated to be about 0.02 per cent. per day.

When this was noticed, the solution was protected from the light and kept under hydrogen in a constant temperature room. The hydrogen was generated from C. P. zinc and sulphuric acid. It was washed by bubbling through solutions of lead nitrate, alkaline potassium permanganate and then through a wash bottle containing some of the arsenious acid solution. To free the solution from air the pressure on the solution was three times reduced as far as possible with a water pump and then the pressure increased to that of the atmosphere by slowly bubbling hydrogen through the liquid.

Instead of using the automatic burette for delivering approximately the required amount of solution, a syphon which could be swung directly over the mouth of a flask upon the balance pan was attached to the stock bottle. The required amount of solution (within from 0.1 to 0.05 grams) was then run into

the flask and its weight carefully determined. It was found that even under these conditions the arsenious acid was oxidizing; the rate was about 0.003 per cent. per day. The rate of oxidation was constant and could be easily followed by standardizing the solution from time to time.

As explained below, the partial pressure of oxygen in equilibrium with such a solution of arsenious acid is surprisingly small, so that if oxidation is to be entirely prevented extraordinary precautions must be taken.

The iodine titrations were completed by means of a dilute solution of arsenious acid. This solution was prepared by diluting about 5 grams of the concentrated solution to exactly 100 times its weight. The burette from which the dilute solution was delivered was calibrated by the use of this dilute solution. On account of the possibility of an error due to the oxidation of the dilute solution a fresh lot was prepared every two or three weeks; the maximum change in strength due to oxidation was estimated to be 0.5 per cent. Practically never was it found necessary to use more than 10 cc. of this solution to complete a titration, and since 1 cc. corresponded to about 0.02 per cent. of the total arsenious acid used in the titration, the error due to the change in strength of the dilute solution was never greater than 0.001 per cent.

The Equilibrium between Arsenious Acid and Oxygen.

The oxidation of arsenious acid may be represented thus,

$$2H_3AsO_3 + O_2 = 2H_3AsO_4 \qquad (1)$$

This reaction may be considered to be the sum of two reactions;

$$2H_3AsO_3 + 2H_2O + 4(+) = 2H_3AsO_4 + 4H^+ \qquad (2)$$

and $$O_2 + 4H^+ + 4(-) = 2H_2O \qquad (3)$$

The electromotive force of the normal arsenious-arsenic electrode (E_2) and of the normal oxygen electrode (E_3) against the normal hydrogen electrode has been calculated to be +0.58 [1] and +1.23 [2] volts respectively. Hence at equilibrium, we have for reaction (1)

$$\frac{RT}{VF} \ln \frac{(H_3AsO_4)^2}{(H_3AsO_3)^2 P_{O_2}} = E_3 - E_2 = +0.65.$$

For this reaction V = 4, hence for room temperature (25° C)

$$\log P_{O_2} = 2\log \frac{(H_3AsO_4)}{(H_3AsO_3)} - 44 \qquad (4)$$

By eliminating H^+ from the equations

$$\frac{(H)(H_2AsO_4)}{(H_3AsO_4)} = 4.8 \cdot 10^{-3}$$ [3]

and $$\frac{(H^+)(H_2AsO_3)}{(H_3AsO_3)} = 6.3 \cdot 10^{-10}$$ [4]

we get $$\frac{(H_3AsO_4)}{(H_3AsO_3)} = 1.5 \cdot 10^{-7} \frac{H_2AsO_4^-}{H_2AsO_3^-}.$$

The substitution of this value for $\frac{H_3AsO_4}{H_3AsO_3}$ in equation (4) gives,

$$\log P_{O_2} = 2 \log \frac{H_2AsO_4^-}{H_2AsO_3^-} - 56 \qquad (5)$$

Either equation (4) or equation (5) may be used to calculate the pressure of oxygen in equilibrium with a solution of arsenious acid part of which has be-

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1) Calculated from results obtained by Mr. Strachan in this laboratory.
2) Abegg, Auerbach and Luther. Messungen electromotorischer Krafte galvanischen Ketten mit wasserigen Elektrolyten. (1911), p. 199.
3) J. Am. Chem. Soc., 30, 35 (1908).
4) Wood, J. Chem. Soc., 93, 411 (1908).

come oxidized to arsenic acid.

For the preparation of the standard arsenious acid solution which was used in this investigation, more alkali was added than was necessary to displace the first hydrogen of the arsenious acid. Hence in the solution all but a negligible amount of the arsenious acid is present as the sodium salt. Similarly the pentavalent arsenic which has been produced by oxidation will be present as sodium arsenate. It was estimated that about two per cent. of the arsenious acid had become oxidized by the time the solution was placed under hydrogen. Hence assuming that in this mixture the two salts are dissociated to the same extent,

$$\frac{H_2AsO_4^-}{H_2AsO_3^-} = \frac{2}{98} .$$

By the substitution of this value in equation (5) the pressure of oxygen in equilibrium with the standard arsenious acid solution used is found to be 10^{-81} atmospheres.

Equation (4) shows that, since arsenic acid is stronger than arsenious acid, the pressure of oxygen at equilibrium may be increased, by increasing the hydrogen ion concentration. It may be shown, however, that even under the most favorable conditions the pressure of oxygen is very small. A 0.3 normal solution of arsenious acid may be prepared without the use of any alkali[1]. In such a solution all but a negligible amount of the arsenious acid will be present as undissociated acid. If two per cent. of this acid becomes oxidized the degree of dissociation of the resulting arsenic acid is from its dissociation constant ($4.8 \cdot 10^{-3}$) calculated to be about 0.6. Hence for

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1) Supersaturated solutions as strong as normal may be kept for sometime, but cannot be depended upon as standard solutions. For the solubility of arsenious acid in water, see Wood. J. Chem. Soc., 93, 411 (1908).

such a solution

$$\frac{(H_3AsO_4)}{(H_3AsO_3)} = \frac{0.4 \cdot 0.006}{0.3} = 8 \cdot 10^{-3} .$$

The substitution of this value in equation (4) shows the pressure of oxygen to be about 10^{-48} atmospheres.

The mechanism of the oxidation is not known, hence it is not possible to determine quantitatively the effect of a change in the partial pressure of oxygen upon the rate of oxidation. It is probable that the rate is influenced by the presence of minute quantities of impurities which act as catalysts. As was mentioned above, when placed under hydrogen the rate of oxidation of the standard arsenious acid solution was about 0.003 per cent. per day and was constant. Hence for the present investigation there was no need to decrease still farther the pressure of oxygen.

Apparatus and Method of Procedure.

The Iodine Coulometer. The iodine coulometer used is shown in figure (2). It consists essentially of two upright limbs connected by a V tube. At the bottom of each limb is placed an electrode. The caps (I) are ground into the upper parts of the limbs. Two short tubes are sealed into the top of each cap; through one runs a glass tube (K) which carries the electrode connection, and through the other a capillary tube (J) which passes through a hole in the electrode to the lowest point of the limb. A short sleeve of rubber tubing (H) is fitted over these tubes, thus making an air tight joint with the cap, and yet permitting the capillary tube, or this and the cap together to be withdrawn without disturbing the electrode. The side tubes (N) with which a levelling bulb may be connected serve for filling the apparatus and for adjusting the level of the solution in the capillary tubes.

The coulometer was supported in a battery jar which was filled with water to the level of the V tube (L) of the coulometer. No attempt was made to keep the temperature of the bath constant, but the arrangement eliminated convection currents and stirring due to sudden temperature changes. A white plate was placed behind the coulometer in order to assist in detecting any diffusion of the iodine solutions.

The Electrodes. Since iodine rather readily attacks platinum, an alloy of platinum and iridium containing about 30 per cent. of the latter was employed for the electrodes. It was found that an electrode of even this composition was attacked when first used, but that after using it as an anode in a strong iodine solution for two or three days, it became passive and no further solution of the metals could be detected. The electrodes however become active again on heating to redness and possibly on standing in nitric acid or cleaning solution. The electrodes were about 6 cm. in diameter and were cut

(see figure) so that they would fold up when being introduced into the limb of the coulometer, and then when in position spread out filling the bulb (M) at the bottom of the limb. To assist in removing the electrode when necessary, a small hole was made in each of the leaflets into which a wire could be hooked. A hole of 0.7 cm. diameter was cut in the center of the electrode, through which the tip of the capillary tube passed.

The electrical connections were made by means of a wire welded on to one of the leaflets of the electrode and sealed into a glass tube which passed out through the cap at the top. In the case of one of the electrodes the connecting wire was woven through some holes in one of the leaflets instead of being welded onto it. This gave greater flexibility and ease of manipulation in introducing the electrode as well as eliminating the danger of breaking the connection, for it was found difficult to make a satisfactory weld between the wire and the electrode both of which consisted of this somewhat brittle alloy. A little paraffin was melted and run down the tube carrying the electrical connections, this served to hold the mercury, which formed part of the circuit, in place when the apparatus was shaken or inverted in order to rinse it out.

Filling the Coulometer. The coulometer is filled by means of the side tube (N) to a little above the level of the V tube (L), with a ten per cent. solution of potassium iodide. Care is taken that no air is entrapped around the electrodes and that no bubbles adhere to their surfaces. The levelling bulb which is attached to the side tube (N) is then raised until the solution rises to the top of the capillary tube (J), which opens rather abruptly into the bulb (G). At the anode side about 25 cc. of a concentrated solution of potassium iodide, (one gram salt to one gram water) previously freed from air by boiling, is run into the bulb (G) and allowed to cover the elec-

trodes to a depth of about 5 cm. During a run the opening E is protected by means of an inverted test tube.

In a similar manner 6 to 8 cc. of the concentrated potassium iodide solution are introduced below the solution in the cathode limb. In the case of the experiments where the amount of iodine formed from iodide ions at the anode is being compared (see p. 6) with that used up at the cathode in producing these ions, the potassium iodide solution is immediately followed by about 45 grams (20 cc.) of the standard solution of iodine in potassium iodide. This is run in from the weight burette, and care is taken that no air is drawn down the capillary. The ground glass joint (B) between the burette and its cap, just fits into the bulb on the capillary at F, the tip of the pipette extends well below this point. As soon as the burette is empty it is withdrawn and the tip protected by means of the glass cap. Loss of iodine from the bulb G is prevented by immediately placing the delivery tube C in position. The ground joint between D and E is lubricated with a little phosphoric acid. In rinsing out the bulb after a run this phosphoric acid is washed into the bulb (G) and then sucked over into the flask in which the titration is performed. The presence of this acid does not affect the titration; in fact it was found that 5 cc. of the acid employed did not affect the result by 0.001 per cent.

The weight burette was filled by suspending it in such a way that the tip of the delivery tube (see A, Fig. 1) of the stock bottle containing the iodine solution was well in the neck of the burette. The solution is then forced over by air pressure. The stop-cock (A) of the burette was lubricated with a drop or two of vaseline. This vaseline had been shaken up with a strong solution of iodine in potassium iodide, let stand during the summer, washed with a dilute sodium thiosulphite solution until it was free from iodine and finally distilled under reduced pressure.

In the experiments where the amounts of iodine formed at the anodes of two coulometers in series were being compared, or where the iodine coulometer was being compared with the silver coulometer, a solution prepared from commercial iodine and potassium iodide was used at the cathode instead of the standard iodine solution. In these experiments the cathode solution was not analysed after the run.

The rate of flow of the solution down the capillary tube was regulated by means of the leveling bulb attached to the side tube N. It was thus found possible to surround the electrodes with the more dense solutions, without causing appreciable mixing of these solutions with the more dilute solution on top.

Removal and Analysis of the Electrode Portions. The current is passed through two iodine coulometers, through a silver coulometer and through a milliammeter in series. This silver coulometer was not handled with any particular care; it was employed in order to calculate the approximate amounts of the arsenious acid solutions to be used in titrating the electrode portions. In the experiments in which the iodine and silver coulometer were being carefully compared, two other silver coulometers were included in the circuit. These are fully described below.

The time required for a run varied from about 15 hours to 65 hours. During this time little mixing of the iodine solution at either electrode with the dilute solution above it occurred. At the anode side no iodine could be detected higher than one-fourth of the distance up the limb. At the cathode side the iodine was rarely visible one-half way up and usually not more than one-third of the way up the limb. The few cubic centimeters of concentrated potassium iodide solution which were run in through the capillary at the cathode were found to diminish materially the migration in this limb. The effect of the added potassium iodide is due to the fact that at the boundary

between the iodine solution and the dilute solution on top, this extra potassium iodide increases the ratio of iodide ions to triiodide ions, and hence the electricity carried, and therefore the distance travelled by the latter under the influence of the current is lessened.

When about 0.05 faraday of electricity have passed, the circuit is broken. The approximate amount of electritity which has passed through the system is calculated from the weight of silver deposited in the silver coulometer, and thus are found the approximate amounts of standard arsenious acid solution necessary to titrate the cathode and anode portions, respectively. A little less (about 0.05 grams) than this amount is then syphoned over into one liter flasks, while they rest on the balance pan. These are immediately stoppered and weighed to one or two tenths of a milligram. The necessary amount of the solution of disodium phosphate is then added and the flasks fitted to the delivery tubes (C) at the anode and at the cathode respectively, in such a way that the tip of the delivery tube is well below the level of the liquid in the flask. On applying a gentle suction to the flask the electrode portion is sucked over through the capillary tube and the delivery tube. The dilute solution of potassium iodide in the limb completely washes the iodine from around the electrode and the latter half of the solution sucked over into the flask shows no color.

The solution in the flask is thoroughly mixed and the titration completed with the dilute arsenious acid solution. Under the conditions employed it was found that equilibrium conditions between iodine and the arsenious acid were attained almost immediately. The reaction between the starch and the triiodide ion is however much slower. Hence in the titrations the dilute arsenious acid solution was added till the solution was no longer colorless; in a good light and with a flask of water as a standard, the dissappearance of

the triiodide ion could be judged to about 0.10 cc. of the dilute arsenious acid solution, i. e., to about 0.002 per cent. As a check, however, 5 cc. of the starch solution was then added, and the dilute iodine solution (0.005 normal) added till on standing for a few moments, the proper pink colored end point remained. This end point was a little more sensitive than the other. About 0.4 cc. of the 0.005 normal iodine solution were required to change from one end point to the other.

Temperature has but a slight effect on the end point. After finishing one of the titrations the solution was warmed to 35° C and the pink colored end point reached. On cooling to 15° C, only 0.15 cc. of the 0.01 normal arsenious acid solution was required to give the same colored end point. This represents a change of 0.003 per cent. for the 20°, hence no attempt was made to regulate the temperature of the solutions during titration.

Standardization of the Iodine Solution. The manipulation employed in determining the ratio of arsenious acid solution to the standard iodine solution is similar to that employed at the cathode in preparation for a run. The coulometer is first filled with a ten per cent. potassium iodide solution. About 20 cc. of a concentrated solution of potassium iodide are then introduced through the capillary tube, as described above (p. 33) and this is followed by 20 - 25 grams of the standard iodine solution from the weight burette. Loss of iodine from the bulb(G)is prevented by immediately placing the delivery tube (C) in position. The iodine solution is allowed to stand over night in the coulometer in contact with the electrode. It is then sucked over as previously described into a solution of arsenious acid and disodium phosphate, and the titration completed with the dilute arsenious acid solution. By thus employing the same manipulation in the standardization as in a run, any constant error should be eliminated; the results show that this is the case.

Standardization of the Arsenious Acid Solution. Two slightly different methods were employed in standardizing the arsenious acid solution against iodine.[1] In the first of these methods about five grams of dry iodine were placed in a previously weighed weighing bottle with a well fitting cap. After weighing again, the bottle was introduced into a flask containing approximately the required amount of the standard arsenious acid solution and was opened below the surface of the solution. In order to duplicate the conditions employed in analysing the electrode portions, and also to hasten the solution of the iodine about 20 grams of potassium iodide were then added. When the iodine had completely dissolved, the required amount of disodium phosphate solution was poured into the flask and the titration completed with the dilute arsenious acid solution.

The employment of the above procedure gave somewhat irregular results, the average deviation from the mean being about 0.015 per cent. It was noticed in these experiments that occasionally particles of solid iodine floated on top of the solution. Thinking that this might cause a loss of iodine, the above method was then somewhat modified. Seven or eight grams of potassium iodide were placed in the weighing bottle and not quite enough water to dissolve this salt was then added. The stoppered bottle was left in the balance case for two or three hours and then weighed. Five or six grams of iodine were then quickly added and the bottle again weighed[2]. It was next introduced into the flask containing arsenious acid and opened under the solution. The results obtained by this method were a little more consistent but on account of the uncertainty due to the loss of water from the weighihg bottle,

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1) For the purification of this iodine see p. 34.
2) The weight of water lost by evaporation from this concentrated solution during the introduction of the iodine was very small; blank experiments showed that it was not over 0.3 mg. and a correction for this loss was applied.

the use of both methods was continued and the average value employed.

The Silver Coulometers.

The quantity of electricity which passed through the system was accurately determined by means of two silver coulometers. There were practically the same type as those employed by Smith, Mather and Lowry, and the various conditions and methods of procedure employed by them were duplicated as closely as possible.

The anodes were of pure mint silver. They were surrounded by filter paper cups, suspended by means of insultated platinum wire.

A 15 per cent. solution of silver nitrate was employed in the coulometers. At the end of every second run the solution was rejected and a fresh lot employed for the next experiment. The silver nitrate was purified as follows; Kahlbaum's salt was dissolved in conductivity water, a large quantity of concentrated nitric acid added and the solution cooled in a freezing mixture, with constant stirring. The silver nitrate thus obtained was thrown on to a Buechner funnel and the excess of mother liquor removed by suction. In this process no filter paper was employed, the first crystals formed a layer on the funnel through which the mother liquor drained. The recrystallization was repeated several times and the final product fused in a porcelain dish until the last traces of nitric acid were driven off. The fused mass was then poured into a platinum crucible floating in a beaker of water. The product obtained by this procedure was perfectly white.

Each of the bowl shaped platinum vessels, which served as cathodes, weighed about 50 grams and was 10 cms. in diameter at the top. Bowl A was 4.5 cms. in depth and held when full 275 cc.; bowl B was 5.5 cms. in depth and held 350 cc. The volumes of silver nitrate solution which were used in

the coulometers during a run were about 150 cc. and 200 cc. respectively.

Before using, the bowls were thoroughly washed with nitric acid and water and dried in an electric oven at 160° C. A third bowl which was of practically the same dimensions and weight and which was used for a counterpoise, was similarly treated. On the completion of a run the electrolyte was removed from the bowls by means of a pipette. They were rinsed five or six times with water and finally filled with water and allowed to stand over night. Three or four more rinsings with water followed after which they were heated in an electric oven at 160° C for one hour. After cooling in a desiccator for several hours they were placed on the balance pan and allowed to come to constant weight. The silver deposit was removed from the bowls by means of nitric acid. The bowls were then thoroughly washed and heated in the oven in preparation for the next experiment.

Weights and Balances. The gold plated brass weights which were used in this investigation were calibrated and standardized by the National Bureau of Standards.

The arsenious acid solution was weighed into liter flasks on a Rueprecht balance, sensitive to 0.1 milligram with this load. All the other weighings were made on a Becker balance sensitive to 0.05 milligrams. A counterpoise was employed in weighing the flasks containing the arsenious acid solution, the burette containing the iodine solution and the platinum bowls which served as silver coulometers.

Except where specified none of the weights are reduced to vacuo. There is no need to reduce the weights of any of the solutions to vacuo since this correction cancels out in the results. The weights of iodine and silver were corrected by subtracting 0.0099 and 0.0031 per cent. respectively from the apparent weights of these elements.

Reproducibility of the Anode Reaction.

Table V shows the agreement obtained between two iodine coulometers in series. All of the data obtained with reference to this point are included in the table. On account of an accident, one of the anode portions in runs 6, 10 and 11, was not titrated. In the calculation of the average deviation from the mean, the results of runs 5, 7 and 8 were not employed. The former was rejected because the deviation was more than four times as great as the average of the others; the results of runs 7 and 8 were not used for the reason explained below. The average deviation from the mean as calculated from the results given in this table is just equal to the uncertainty in judging the end point, (see p. 36).

Permissible Current Density. The object of runs 7 and 8 was to make certain that the current densities employed were not too large. In these runs, in one coulometer was employed an anode of the usual size (28 sq. cm.) while the surface of the second was but 4 sq. cm. In these two experiments the larger electrode gave the greater amount of iodine. The deviations are but slightly greater than the average of the other experiments, and the result obtained from but two runs cannot be regarded as conclusive. It will be seen however that a current density of 0.01 amperes per sq. cm. is allowable; in all the runs except these two the current density was between 0.0007 and 0.003 amperes per sq. cm. and hence well below this possibly limiting value.

TABLE V

Reproducibility of the Anode Reaction.

No.	Date	Current in Milliamperes	Grams of Arsenious Acid Solution. Anode No. 1.	Anode No. 2.	Mean	Deviation from the Mean. Per cent.
1	Mar. 4	37	58.6584	58.6598	58.6591	0.0012
2	6	40	52.6863	52.6841	52.6852	0.0021
3	9	20	57.2651	57.2622	57.2641	0.0025
4	11	40	55.1379	55.1404	55.1391	0.0023
5	16	40	60.7797	60.7682	60.7740	(0.0095)
7	21	43	65.5012	65.4968	65.4990	(0.0032)
8	23	68	63.3568	63.3517	63.3542	(0.0040)
9	Apr. 7	45	65.2055	65.2100	65.2077	0.0035
12	20	70	62.2437	62.2415	62.2426	0.0018
13	27	80	59.8340	59.8345	59.8342	0.0004
					Average deviation from the Mean	0.0020

Standardization of the Iodine Solution.

The results which were obtained from time to time in the comparison of the concentrated iodine solution with the standard arsenious acid solution are given in Table VI. In the first column is given the number of the comparison, in the second the date on which the arsenious acid solution was drawn from the stock bottle for immediate use. The third and fourth columns give the weights of the iodine and arsenous acid solutions respectively which were used. The number of grams of arsenious acid solution required to titrate one gram of the iodine solution is given in the fifth column. In the sixth column is given this value as calculated for the day in question (see below). The seventh column contains the percentage difference between this ratio as found and as calculated.

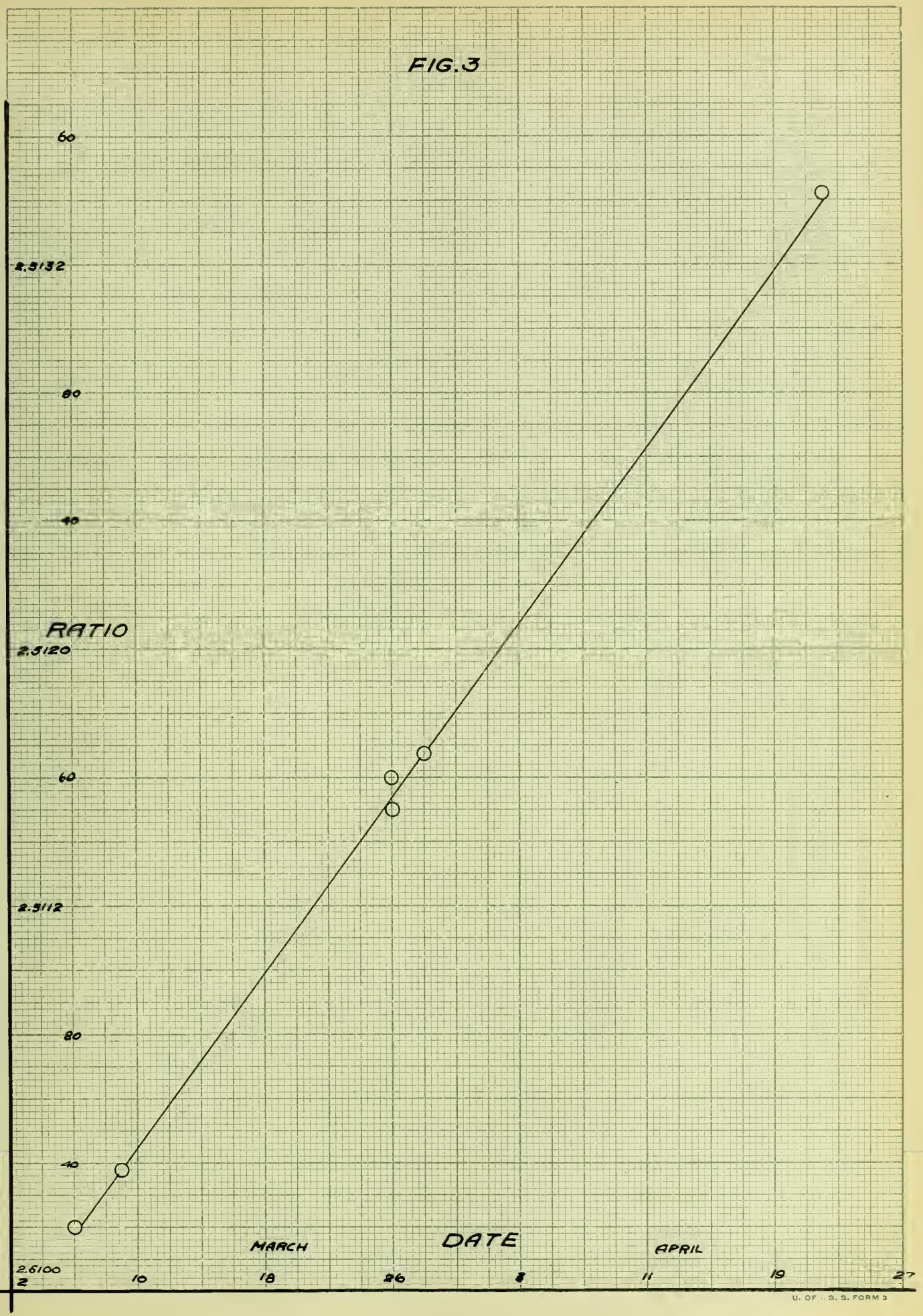
The rate of oxidation ($\frac{dC}{dt}$) of the arsenious acid solution is given by the equation

$$\frac{dC}{dt} = k(C_{As})^m (C_o)^n$$

where C_{As} is the concentration of the arsenious acid in the solution, C_o is the concentration of the dissolved oxygen and m and n are constants depending upon the mechanism of the reaction. Since the rate of oxidation was found to be extremely slow the concentration of the arsenious acid may be considered to be constant. In order to detect any change in the rate of oxidation due to a change in the partial pressure of the oxygen or to any other cause, the ratio of the arsenious acid solution to that of the iodine solution was determined over a period of 47 days. The rate of oxidation was found to be constant.

The ratio of the two solutions as determined at various times was plotted as ordinates and the time (day of month) as abscissae (see Fig. 3). The best

FIG. 3



U. OF I. S. S. FORM 3

straight line was then drawn through the points and its slope, i. e. the rate of oxidation determined. The solution was found to be oxidizing at the rate of 0.00273 per cent. per day. The calculated value of the ratio of the two solutions at any given time (see column six, Table VI) was read off from the curve; it was estimated to be known to 0.001 per cent.

In calculating the average deviation from the mean the results of standardizations 3 and 4 were rejected. The former because it was subsequently found that the potassium iodide used in making up the solutions for the coulometer, already contained some iodine. The result of standardization 4 was rejected because the deviation from the mean was more than four times as large as the average of the deviations of the results of the experiments.

TABLE VI

Ratio of the Arsenious Acid and Iodine Solutions.

No.	Date	Weight of Iodine Solution, Grams.	Weight of Arsenious Acid Solution, Grams.	Ratio Found	Ratio Calculated	Difference per cent.
1	Mar. 6	20.3883	51.1787	2.51020	2.51017	0.0012
2	9	23.0459	57.8530	2.51038	2.51038	0.0000
3	11	19.1883	48.1824	2.51105	2.51055	(0.02)
4	19	21.9252	55.0480	2.51080	2.51105	(0.01)
5	26	26.0033	65.3085	2.51160	2.51154	0.0024
6	26	23.0414	57.8686	2.51150	2.51154	0.0016
7	28	27.0322	67.8960	2.51167	2.51167	0.0000
8	Apr. 22	24.6357	61.9202	2.51342	2.51339	0.0012
				Average deviation		0.00106

Comparison of the Reactions at Anode and Cathode.

For the purpose of comparing the amount of iodine formed at the anode with the amount which disappears at the cathode, a series of runs were made in which the current was passed through two iodine coulometers connected in series. The anode portions from both coulometers were then titrated as was also the cathode portion from one of them, that from the other being rejected [1].

In Table VII are given the results of these comparisons. In the first column is given the number of the run, in the second column the day on which the arsenious acid solution was withdrawn from the stock bottle, and in the third column the current in milliamperes. The next column gives the weight of the concentrated standard iodine solution which was run down the capillary tube into the cathode limb. The fifth column gives the mean weight of arsenious acid solution used to titrate the anode solutions (see Table V). The weight of arsenious acid solution required for the cathode portion is given in column six. The next column gives the total amount of arsenious acid solution used in titrating cathode and anode portions. The eighth column gives the quantity of this solution which should be required for the titration as calculated from the weight of iodine solution used and the ratio of the two standard solutions as read off from the curve (Fig. 3).

The results show that, within the limit of error of the analysis, the same amount of iodine is formed from iodide ions at the anode as is formed into iodide ions at the cathode. And that hence either reaction in the iodine coulometer is a perfectly clean cut one and hence suitable for the determina-

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1) This was necessary because only three suitable electrodes were available at the time these comparison runs were made.

tion of the true value of the faraday. Since the reaction at the anode is much more easily studied and since the manipulation is much simpler, the anode portions only were analysed in the experiments to be described below in which a preliminary comparison of the iodine and silver coulometers is made.

TABLE VII

Comparison of Anode and Cathode Reactions

No.	Date	Current Milliampere	Weight of Iodine Solution, Grams	Weight of Arsenious Acid Solution Grams Anode	Cathode	Total found	Total Calc.	Deviation Per cent.
2	Mar.6	40	47.0374	52.6852	65.4103	118.0955	118.0719	(+0.020)
4	11	40	45.6123	55.1391	59.3737	114.5128	114.5100	+0.0024
5	16	40	45.4523	60.7740	53.3585	114.1325	114.1238	+0.0076
6	19	20	44.6216	48.3080	63.7373	112.0453	112.0471	-0.0016
7	21	43	45.6662	65.4990	49.1721	114.6711	114.6763	-0.0044
							Average Deviation	0.0040

Comparison of the Iodine and Silver Coulometers and the Determination of the Faraday.

In this series of experiments a current of electricity was passed through two iodine coulometers and two silver coulometers connected in series. The silver coulometers and the method of treating them has been described in detail on page 38.

During the progress of this series of experiments, the arsenious acid solution was frequently standardized against iodine. The procedure employed has been already described, (p. 37). Table VIII gives the results of these standardizations. The figures in the fifth column under grams arsenious acid solution per gram iodine, calculated to April 14th, were obtained from those of the previous column by correcting for the rate of oxidation of the arsenious acid; 0.00273 per cent. per day (see above p. 43). All of these values were calculated to the same day in order to compare them with one another and to use the final value in connection with the results obtained by the aid of the silver coulometer.

TABLE VIII

Standardization of Arsenious Acid Solution.

Date	Wt. of Iodine cor. to vacuo, Grams.	Wt. of Arsenious Acid Solution, Grams.	Grams Arsenious Acid Soln. per gram Iodine Found	Calc. to Apr.14	Deviation from Mean Per cent.
Apr. 9	4.37000	42.6330	9.0134	9.0146	0.012
9	6.08670	54.8667	9.0142	9.0154	0.003
10	5.03120	45.3625	9.0162	9.0172	0.018
10	4.19525	37.8096	9.0122	9.0132	0.027
16	8.17160	73.6790	9.0165	9.0160	0.004
24	5.28225	47.6270	9.0164	9.0140	0.018
26	6.88315	62.0797	9.0189	9.0160	0.004
26	4.66625	42.0788	9.0177	9.0148	0.009
29	7.05620	63.6516	9.0206	9.0169	0.014
29	6.13420	55.3434	9.0221	9.0184	0.030
			Mean	9.01565	
			Average deviation from Mean		0.014

Table IX gives the results of the determinations of the electrochemical equivalent of iodine and of the faraday. The amount of electricity which passed through the system was measured by means of the silver coulometer and its value in coulombs was calculated by dividing the corrected weight of silver (column six) by 0.00111827, which Smith, Mather and Lowry found to be the increase in weight of the cathode bowls per coulomb, under similar conditions. In order to calculate the amount of iodine formed, the amount of arsenious acid solution which was required for the titration was calculated to April 14th, by correcting for the rate of oxidation. The result is given in column nine. The number of grams of iodine formed were then calculated by dividing these values by 9.01565, the number of grams of arsenious acid solution corresponding to one gram of iodine (see Table VIII). The electrochemical equivalent as given in the tenth column was found by dividing the number of grams of iodine formed by the number of coulombs of electricity which had passed. The corresponding values for the faraday were obtained by dividirg the results in column ten into the atomic weight of iodine, 126.913[1] .

The chief sources of uncertainty in the value of the faraday are due to the error in measuring the current and to the uncertainty as to the exact strength of the arsenious acid solution. The necessity of very close duplication of conditions and procedure in using the silver coulometer was mentioned above. It is believed however that the current was known to 0.025 per cent. The value given for the current is likely to be too great rather than too small, because practically all disturbing influences cause an error in this direction.

The other source of uncertainty arises from the irregular results obtained in standardizing the arsenious acid solution against iodine. The final

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1) Baxter, J. Am. Chem. Soc., 32, 1602 (1910).

TABLE IX

Electrochemical Equivalent of Iodine and the Value of the Faraday.

No.	Date	Current in Milliamperes	Silver Deposited in Coulometer Bowl A	Bowl B	Mean in Cor. to Vacuo	Coulombs	Arsenious Acid Solution Used	Calc. to Apr. 14	Iodine Grams	Electrochemical Equivalent of Iodine, Milligrams per Coulomb.	Faraday Coulombs.
9	Apr.7	45	6.15230	6.15285	6.15239	5501.72	65.2077	65.2201	7.2341	1.31488	96,520
10	10	50	6.50800	- - -	6.50779	5819.52	68.9599	68.9674	7.6487	1.31433	96,560
11	14	40	5.94555	5.94500	5.94510	5316.35	63.0049	63.0049	6.9884	1.31414	96,575
13	27	80	- - -	5.64250	5.64232	5045.58	59.8342	59.8119	6.6342	1.31480	96,525
										Mean	96,545
										Average Deviation	0.024 o/o

Summary and Conclusion.

1. The various values which have been calculated for the faraday by means of different coulometers are discussed. It is pointed out that the weight of the silver deposited in the silver coulometer is particularly sensitive to changes in conditions, and that it is not possible to study the effect of the electrochemical reaction alone.

2. It is doubtful if the electrochemical reaction in the silver coulometer is reversible. In order to determine the true value of the faraday a reaction which is reversible must be employed.

3. An element which is not deposited but is liberated in the solution offers particular advantages for this purpose, since errors due to inclusion, adsorption, etc. are not present.

4. The reaction involved in the iodine coulometer appears to constitute an ideal electrochemical reaction to be used in the determination of the faraday.

5. It is found that the amount of iodine formed at the anode of the iodine coulometer can be determined to within 0.002 per cent., and that the amount of iodine formed in two coulometers in series agrees within this limit of error.

6. The reversibility of the iodine-iodide electrode has been tested, and a coulometer devised which will carry a current of at least 0.08 amperes for 18 hours. It is found that the amount of iodine in the coulometer after the passage of the current is within 0.004 per cent. of the amount originally introduced at the cathode.

7. By a comparison of the silver and iodine coulometers the preliminary value, 96,545 $\pm$ 30 coulombs has been found for the faraday.

value should not be in error by more than 0.01 per cent. however. If anything the strength of the solution is over-estimated, because iodine was possibly lost during the standardization (see p. 37). These two errors have opposite effects upon the value of the faraday as given in Table X and tend to counteract one another. The uncertainty in the value, 96,546 coulombs, is estimated to be about 0.03 per cent.

This value for the faraday is, of course, not in agreement with the value as calculated by means of the silver coulometer, but is in good agreement with the value obtained by the use of other coulometers; in fact it lies between that calculated from the investigation of Richards and Heimrod on the copper coulometer (96,535) and that calculated from the result of Gallo's investigation of the iodine coulometer (96,560). It is interesting to note that all other elements give a greater value than does silver. There can scarcely remain much doubt but that the value of the faraday at present accepted (96,473) is at least 0.05 per cent. too small.

Biographical.

The writer received his elementary and secondary education in the schools of Toronto. He entered McMaster University, Toronto, in the fall of 1903 and graduated with the degree of Bachelor of Arts in 1907. During the course he took special work in the departments of Chemistry and of Mathematics, and was awarded two scholarships in the latter department. After spending a year in the laboratory of the Comfort Soap Works, Toronto, the writer returned to McMaster University, and in 1909 received the degree of Master of Arts in Chemistry. The following year he was research assistant at the same institution. During the college years 1910-11 and 1911-12 he has held a fellowship in the Department of Chemistry at the University of Illinois.

The writer is a member of Sigma Xi, and of Phi Lambda Upsilon Societies and of the Gamma Alpha Graduate Scientific Fraternity.

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Action of Amines on Dibasic Aliphatic Acids. J. Am. Chem. Soc., 31, 1233 (1909).

Action of Amines on Phthalic Acid. J. Am. Chem. Soc., 32, 1319 (1910).

Derivatives of Camphoroxalic Acid. J. Am. Chem. Soc., 32. 1499(1910).

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